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Pressure-induced Trap-door Ion-Exchange in a Zeolite

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Beamline(s): X7A

Pressure-induced volume expansion, observed in several zeolitic and other framework materials, opens a unique opportunity towards novel chemical applications. For natrolite, which undergoes a reversible volume expansion around 1.2 GPa,[1] the expanded pore openings through the channel swelling under pressure may dramatically alter the ion exchange and other sorption properties of this small-pore zeolite. In an attempt to test this hypothesis, we have used a Cd-containing fluid as a pressure-transmission media and repeated the high pressure experiment. The material showed a two-step volume discontinuity under increasing pressures, and Rietveld refinements using these data revealed Cd-exchange occurs through the intermediate, larger-volume phase between 0.8 and 1.2 GPa, which also contains 50% more water molecules than the original phase below 0.8 GPa. The Cd-exchange level was refined to be 50%, which is about 5 times greater than the maximum exchange level achievable under ambient conditions.[2] Above 1.2 GPa, the Cd cations become statistically disordered with Na cations, and the channel water content doubles compared to the original phase. Upon pressure release, the Cd cations are retained within the channel sites although the changes in the channel water contents are reversed. This constitutes the first pressure-driven trap-door ion exchange in a zeolite, and further characterization of the pressure-recovered sample is underway to confirm the result.

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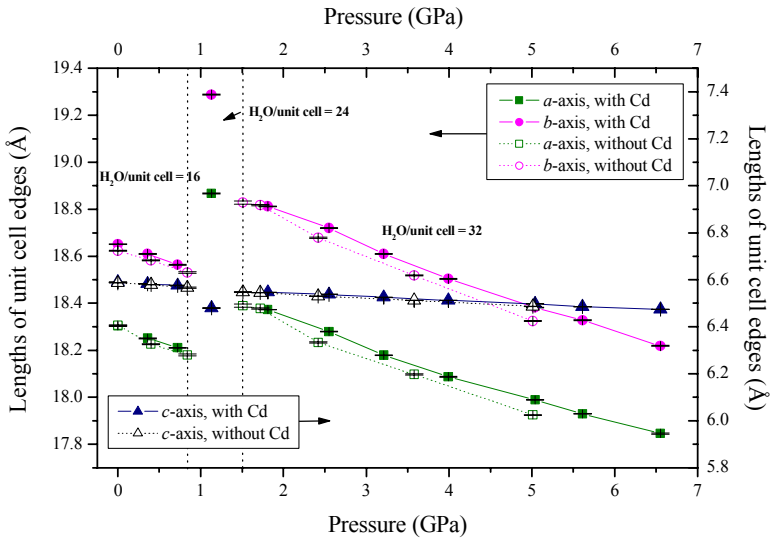
References:

[1] Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Artioli, G. Journal of the American Chemical Society 2002, **124**, *5466-5475*.

[2] Dyer, A.; Faghihian, H. Microporous and Mesoporous Materials 1998, **21**, *27-38*.



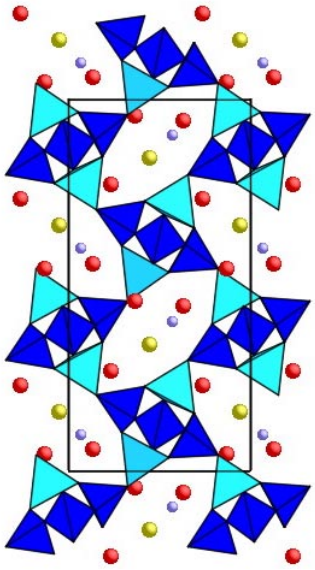


Figure. Pressure dependence of the unit cell edge lengths of natrolite (left). Polyhedral representations of Cd-exchanged natrolite at 1.1 GPa (right). Tetrahedra are shown in two colours to illustrate the ordering of Al/Si over the framework tetrahedral sites. Small-silver balls represent Cd, larger-yellow balls for Na, and water molecules are shown in red balls. Straight lines define a unit cell.